

Informal Translation

Patent EP 0 121 089 B1

Description

The invention concerns motor fuel and a process to produce it consisting of a base hydrocarbon or primarily hydrocarbon fuel together with the addition of alcohols and/or ethers and/or ketones as well as additives which may be water and aromatics.

The use of methanol and ethanol as additives in conventional fuels is known. Also the addition of mixtures of methanol and tert butanol is known.

The problem of using such fuels is only partly solved so that their introduction into general use is still not possible. On the other hand the economic advantages of using alternative fuels is becoming increasingly important.

The problems consist particularly in the phase separation into alcohol and hydrocarbon phases especially at low temperatures and humid conditions, although in this case there has been some advance in the addition of methanol by simultaneously adding tert butanol as well. Butanols, being obtained from the C4 fraction of ethylene plants and only then when naphtha or medium oils are used, are not abundantly available and at relatively high cost. The use of an alternative fuel depending on a relatively high proportion of butanol is consequently rather restricted.

Other existing problems are the optimal carburetor parameters, flashpoint, density and bubble formation at high temperatures. Although the addition of pure ethanol to normal fuels in contrast to methanol leads to fewer problems, it is still not possible to use ethanol fuels in general practice which are risk free and which adhere to the ***DIN Norm 51600¹***. In particular this is not possible in the case of non-absolute ethanol, which contains approximately 4.4 % by volume as a result of the formation of the ethanol water azeotrope during distillation. It is even less possible for ethanol which contains more water than that in the azeotrope at atmospheric pressure.

Economically it is of great interest to be able to mix non-absolute ethanol, especially bioethanol, with standard fuels and to have an easily available alternative fuel based on the growing domestic raw materials meeting all the demands.

The distillation of ethanol water mixtures at atmospheric pressure in a distillation column consists of 95.57 % by volume ethanol and 4.43 % by volume water at the minimum evaporation point of 78.15 deg C.

So called bioethanol is produced from natural products such as fruit, grain, potatoes, other natural, sugar containing products and also cellulose and sulphites. During processing for ethanol, which is particularly dilute, an ethanol is produced containing more water than the ethanol water azeotrope. The separation apparatus, also known as a still, can be operated continuously or in batch. Often they have at the top of the column

¹ This is the DIN norm for super gasoline [translator's note]

so called amplication columns. Depending on the design the distillation effect results in an ethanol with up to 25 % by volume water content.

Bioethanol is distilled with a rather small amount of apparatus and energy. *Since such biethanols contain organic contaminants such as aldehydes, ketones, acids and esters, their use as additives in gasoline has been considered impossible.* In addition there are problems related to mixing at environmental temperatures because of the high water content which are considered as uneconomically solvable.

A typical bioethanol for example has the following properties:

Ethanol	78.5	weight %
Water	21.4	weight %
Density	0.8482	g/cm³
Aldehyde	0.10	weight %
Ketone	0.10	weight %
Ethylacetate	0.10	weight %
Acids	23	ppm
Condensation	60	ppm
Citric acid	2.3	mg/l

Attempts to use pure ethanol in fuels have not lead to any particularly useful fuel because of the relatively high costs and lack of suitable distribution system. Nor is this to be expected soon. In addition there are problems with cold start, safety considerations against explosions or the problem of bubble formation at high temperatures during engine operation. Finally there is not enough ethanol in Europe.

The goal of this invention is to produce a fuel which avoids the stated problems, fulfills fuel norms, takes the suitability of additives into consideration and can be offered without restriction at gas stations.

The inventive step consists in finding a new fuel which is based on standard hydrocarbon or predominantly hydrocarbon fuel with additives of alcohols and/or ethers and/or ketones as well as aromatics, with water in addition with 0-10 % by volume ethanol – water mixture containing more water than the azeotrope, 0-10 % by volume butanol and 0-5 % by volume methanol and/or 0-15 % by volume methyl tert butyl ether and/or 0-15% by volume acetone.

After a number of laboratory and engine tests it was established that *the invented fuels are excellent for engines which can be mixed with existing fuels, fulfilling the DIN norm* and which can be offered to drivers.

The invented fuel contains 0-10% by volume ethanol with a higher water content than that found in the ethanol water azeotrope, but can also contain parts of pure ethanol and/or ethanol water azeotrope and/or ethanol or technical ethanol with less water. The preferred embodiment uses 0-5 % by volume bioethanol. Additionally, 0-5 % by volume

methanol can be used, which can be technical undistilled methanol or {abgetopptes} technical undistilled methanol. ***In the last case some of the contaminants of the methanol are removed through the head.*** Further uses according to the invention are bioethanol combined with butanols from which tert butanol is preferred, although butanol mixtures can also be used, methyl tert butyl ether and acetone. Additional mixtures can contain in certain amounts other ethers such such as dimethyl, diethyl, methyl tert amyl ether and aromatics. Also further water can be added. The acetone can be pure, technical or bioacetone.

According to claim 1 bioethanol can be combined according to the invention with

- a) butanol, methanol, methyl tert butyl ether, acetone
- b) butanols, methanol, methyl tert butylether
- c) butanols, methanol, acetone
- d) butanols, methyl tert butyl ether, acetone
- e) butanols, methyl tert butyl ether
- f) butanols, acetone
- g) butanols

The base hydrocarbon component preferably conforms with the fuels norms for super gasoline or regular gasoline or mixtures of the same. The base hydrocarbon component can contain additives which may include methanol from 0-5 % by volume and/or butanols from 0-10 % by volume whereby these are to be taken into account by the addition according to the invention of bioethanol.

Additives which can be used include a large number of such which are on the open market such as Keropur from BASF. ***Also lead in the form it is usually used in fuels can be added.***

Although the components can be mixed together such that one obtains a high octane super gasoline fuel or a lower octane regular gasoline with bioethanol, methanol, butanols, methyl tert butylether, acetone and other additives; it has nevertheless been found that the preferred method is to mix super gasoline and/or regular gasoline which may already have 0-5 % by volume of methanol and 0-10 % by volume of butanols with a premixed component, which contains bioethanol, butanols, and/or methanol and/or methyl tert butylether and/or acetone and possibly additives and lead compounds.

The results show that in this way a particularly effective and economical mixture of the components is possible and that fuel currently on the market already containing methanol and/or butanols can be used for the production of the fuels according to the invention.

The process for producing fuels according to the invention is supported by the following examples.

Example 1

A typical mixture according to the invention has for example the following formula:

50 % by volume	ethanol (78 weight %)
50 % by volume	tert butanol
0.15 g/l	lead
0.25 g/l	additive

This mixture was added to super gasoline having 3% by volume of methanol and 2 % by volume of tert butanol, where 2 % of the ethanol additive was mixed with 98 % of super gasoline.

Example 2

A mixture was produced from the following components

14.2 % by volume	ethanol (80 weight %)
42.9% by volume	methanol
42.9% by volume	tert butanol
0.15 g/l	lead
0.08 g/l	additive

This mixture was added to super gasoline having no methanol or butanol additives, where 7 % of the ethanol additive was mixed with 93 % of super gasoline.

Example 3

A mixture was produced from:

30 % by volume	ethanol (90 weight %)
30 % by volume	butanol blend (3 weight % n-butanol, 42 weight % isobutanol and 55 weight % tert butanol)
10 % by volume	acetone
30 % by volume	methanol
0.2 g/l	additive

This mixture was added to a mixture of 80 % by volume super gasoline and 10 % regular gasoline so that a mixture of 90 % by volume super / regular gasoline and 10 % by volume of oxygen containing mixture was obtained.

Example 4

A mixture was produced from:

25 % by volume	ethanol (85 weight %)
25 % by volume	tert butanol

20 % by volume	methanol
25 % by volume	methanol tert butyl ether
5 % by volume	acetone
0.25 g/l	additive

This mixture was added to super gasoline so that the mixture of 90 % by volume super gasoline and 10 % by volume of oxygen containing compounds was obtained.

Example 5

92 % by volume regular gasoline was mixed with 1.5 % by volume ethanol (80 weight %), 2.5 % by volume butanol and 4 % by volume methyl tert butyl ether.

A bioethanol super gasoline according to the invention has the following characteristics:

<i>Density d15</i>	<i>0.743 g/cm³</i>
Octane number	
ROZ	99.4
MOZ	88.8
FOZ	93.3
Lead content	0.13 g/l
Evaporation	
<i>At 70 deg C</i>	<i>41.0 % by volume</i>
<i>At 100 deg C</i>	<i>59.5 % by volume</i>
<i>At 180 deg C</i>	<i>97.0 % by volume</i>
Upper boiling point	200 deg C
Residue	1.0 % by volume
Vapor pressure (RVP)	830 mbar
Water	2790 ppm
Methanol	3 % by volume
TBA content	3 % by volume
Ethanol (78.5 weight %)	1 % by volume
Cloud point	-20 deg C
Copper strip test	< 1
Induction time	> 720 min.
S {acid} content	< 0.001%

To a person ordinarily skilled in the art it was surprising to find that the fuels according to the invention had appreciably less carbon monoxide emissions than normal fuels. At the same time it was established that at lower and middle revolutions there was better torque with a softer engine cycle.

The experiments of the claimant have lead to a novel result in that ethanol, which contains a higher water than that of the ethanol water azeotrope at atmospheric pressure without the need for any special purification of this technical ethanol, can be added

according to the invention to normal fuels in such a way that the driver has new fuels available with the characteristics of conformance to norms, environmentally friendly, availability of the components, use in standard engines and vehicles, technically problem free production and mixing of fuels according to the invention, compatibility with existing norm conforming fuels and unrestricted mixability without danger of phase separation.

This invention is of great importance with respect to reducing the dependence on imported mineral oils as it enables for the first time the addition of bioethanol produced with relatively low energy requirements to fuels. The comprehensive tests of the claimant teach that the contaminants in this alcohol do not cause damage to the engine nor to the environment.

Claims

[See patent for claims in English.]